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Determination of CO<sub>2</sub> in air using the NOAA manometer  
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## Determination of CO<sub>2</sub> in air using the NOAA manometer

GMD Technical Procedure

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### 1. Purpose

This document provides the technical procedure for the determination of carbon dioxide (CO<sub>2</sub>) in air using the NOAA manometer. Dry-air mole fractions are traceable to the SI base units mass and temperature.

### 2. Scope

This document provides general procedures for the measurement of CO<sub>2</sub> primary standards. The NOAA manometer is the principal method for determining the CO<sub>2</sub> mole fractions in CO<sub>2</sub> primary standards. The primary standards are used to assign mole fractions to secondary standards via scale transfer using NDIR methods. Detailed descriptions of the manometer and manometric method are given by Zhao et al. (1997).

### 3. Informative References

JCGM (2012), International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 200:2012 (JCGM 200:2008 with minor corrections).

JCGM 100:2008 Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement (ISO GUM 1995 with minor corrections), Joint Committee for Guides in Metrology (2008); [http://www.bipm.org/utis/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf)

Sengers, J. M, H.L. Klien, and J. S. Gallagher, Pressure-volume-temperature relations of gases; virial coefficients, Report AEDC-TR-71-39, Heat Division, National Bureau of Standards, Gaithersburg, MD., 1971.

Zhao, C. L., P. P. Tans, and K. W. Thoning, (1997), A high precision manometric system for absolute calibrations of CO<sub>2</sub> in dry air, *J. Geophys. Res.*, 102, D5, pp. 5885-5894.

Zhao, C. L. and Tans, P. P. (2006), Estimating the uncertainty of the WMO mole fractions scale for carbon dioxide, *J. Geophys. Res.*, 111, D08S09, doi:10.1029/2005JD0060003.

### 4. Terms and Definitions

**analyte:** A substance whose chemical composition is to be determined by chemical analysis.

**calibration episode:** The period during which WMO/GAW primary standards are analyzed using the manometer (normally 6-12 months duration).

**large volume (LV):** A glass volume of approximately 7 L, located inside a temperature-controlled oven.

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**manometer:** A device used to determine the mole fraction of CO<sub>2</sub> in air. The manometer consists of two glass volumes (SV and LV), a glass vacuum manifold for separating CO<sub>2</sub> from other components in air, various valves, pressure transducers, and temperature sensors, and a temperature-controlled oven..

**mole fraction:** The ratio of the number of moles of analyte to the total number of moles (expressed as  $\mu\text{mol mol}^{-1}$ , or ppm for CO<sub>2</sub>). Dry air mole fraction is the ratio of the number of moles of analyte to the total number of moles in dry air. Within the scope of this TP, all samples are analyzed for dry air mole fraction.

**NDIR:** Non-Dispersive Infra-Red (analyzer).

**primary standard:** A measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention. For GMD, CO<sub>2</sub> primary standards are aluminum cylinders containing dry air, for which the CO<sub>2</sub> mole fraction has been determined using the manometer.

**small volume (SV):** A glass volume of approximately 8 cm<sup>3</sup>, located inside a temperature-controlled oven.

**volume ratio:** Ratio of volumes LV/SV.

## 5. Procedures

### 5.1 CO<sub>2</sub> Primary Standards

CO<sub>2</sub> primary standards are intended for long-term use, stored in a secure location, and used sparingly to transfer the CO<sub>2</sub> scale to secondary standards. CO<sub>2</sub> mole fractions are determined using the manometer approximately every two years. The timing of manometer measurements is not critical, as long as it is sufficient to determine long-term drift.

### 5.2 Gas Handling

Prior to analysis, a primary standard is moved to the manometer laboratory. A regulator is attached and flushed several times with gas from the cylinder. It is left to the analyst to determine that the regulator connection is leak-free, and that the regulator volume is sufficiently flushed.

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### 5.3 Manometer Operation

The theory behind the manometer is that the mole fraction of CO<sub>2</sub> in an air sample can be determined by measuring the pressure and temperature of nearly pure CO<sub>2</sub> in a known volume extracted from the sample, and the pressure and temperature of the air sample in a larger volume prior to extraction. The two volumes need not be known absolutely, as long as the ratio of volumes can be determined.

The manometer consists of a glass manifold with computer-controlled valves, a vacuum pump, a data acquisition system, and high-precision pressure and temperature sensors. A computer program controls the evacuation of the manifold and sample volumes (LV, SV) and the filling of the large volume with sample gas. CO<sub>2</sub> is extracted from the large volume, cryogenically purified to separate CO<sub>2</sub> from other atmospheric constituents, including water vapor, and cryogenically transferred to the small volume upon which the temperature and pressure of the nearly pure CO<sub>2</sub> is measured.

The steps in the procedure are as follows:

- 1) A gas cylinder (sample gas) is connected to an inlet port.
- 2) The regulator is flushed several times to purge room air and checked for leaks.
- 3) The “PREPARE” program is run to prepare the manometer an experiment (note 1)
  - a. The manometer is evacuated.
  - b. The large volume is filled with sample gas and allowed to equilibrate for several hours (3-4 hours is usually sufficient).
- 4) The “MANO” program is run to perform a manometer experiment
  - a. The manometer is evacuated.
  - b. The large volume is filled with sample gas.
  - c. The large volume is flushed with sample gas for a few minutes.
  - d. The CO<sub>2</sub> in the sample gas is measured continuously, both by flushing gas through the LV and by diverting gas directly to the analyzer (by-passing the LV). This is a quality control indicator. If the CO<sub>2</sub> mole fractions differ, it is likely that the surfaces in the manometer have not reached equilibrium and the manometer needs to be evacuated and re-filled. The amount of CO<sub>2</sub> difference that can be tolerated is a matter of experience and is left to the analyst.

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- e. After filling the LV and allowing for stabilization (~5 min.), the pressure and temperature are measured and recorded.
  - f. After evacuating the extraction manifold, CO<sub>2</sub> is cryogenically extracted from the sample in the large volume. Flow rate and pressure are controlled to extract all CO<sub>2</sub> while preventing any condensation of liquid oxygen. This is a multi-stage process designed to separate CO<sub>2</sub> from other constituents, including water vapor.
  - g. The purified CO<sub>2</sub> is cryogenically transferred to the small volume.
  - h. The CO<sub>2</sub> is allowed to vaporize.
  - i. The pressure and temperature of the small volume are measured and recorded as the temperature of the oven stabilizes. Data should be collected for at least 30 minutes to ensure that the temperature equilibration of the small volume is observed.
  - j. The mole fraction of CO<sub>2</sub> for a particular run is determined from the broad maximum in calculated CO<sub>2</sub> mole fraction that occurs approximately 15 minutes after the CO<sub>2</sub> is isolated in the small volume. Corrections for N<sub>2</sub>O are applied, since N<sub>2</sub>O is also trapped along with CO<sub>2</sub>.
- 5) After the experiment is complete, the manometer is flushed and evacuated to prepare for the next analysis using the “FLUSH” program

Notes: (1) We have found that repeatability improves when the PREPARE step is run twice: once the night before a planned run, and once the morning of the planned run.

## **5.4 Traceability**

Temperature sensors critical to the manometer operation are calibrated by an accredited calibration and testing laboratory approximately every two years. The testing laboratory's Accreditation Body is covered by the ILAC Arrangement. The pressure sensor is calibrated in-house, at intervals determined by the analyst, using a dead weight piston gauge. The mass set, vacuum gauge, and piston area (including thermal and elastic expansion coefficients) should also be calibrated by an accredited calibration and testing laboratory at intervals similar to the temperature probes. It is preferred, but not always practical, to send devices for calibration prior to measuring the suite of primary standards. In the event that the manometer is used prior to full calibration, data should be stored to allow reprocessing using updated coefficients.

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Prior to and during a calibration episode, the pressure sensor should be calibrated several times using the dead weight piston gauge. It is left to the analyst to determine suitable calibration coefficients for the pressure sensor, and how they might change with time.

Although the volume ratio is a fixed physical quantity, it is recommended that the volume ratio be confirmed by experiment before and during the calibration episode. The volume ratio is measured by successive expansions of air, argon, or N<sub>2</sub> into progressively larger volumes bridging the volume difference between the SV and LV. Care should be taken to ensure that the volume ratio remains constant: the physical state of the manometer (connections, glassware, valves, etc.), should not be altered during a calibration episode unless necessary. Any alteration of the physical state of the manometer should be followed by a rigorous assessment of the volume ratio.

Multiple sensors are installed such that there is redundancy in the in-house calibration of critical elements (volume ratio, main pressure gauge, temperature sensors). Between accredited calibrations of the equipment, experiments can be performed to check the performance of critical elements. These include, but are not limited to:

- comparison of all temperature probes in a common location in the manometer oven
- comparison of multiple vacuum gauges
- comparison of the main pressure sensor with other high-quality sensors
- testing the sensitivity of the system to errors in various devices
- measurement of several well-characterized air samples in gas cylinders to aid in assessing performance of the entire system, since drift is unlikely to be consistent among multiple gas cylinders

## 6. Calculations

### 6.1 Dry Air Mole Fraction

The mole fraction of CO<sub>2</sub> is determined from the measured pressure, temperature, and volume of the extracted CO<sub>2</sub> (SV) and the measured pressure, temperature, and volume of the air sample (LV). Because N<sub>2</sub>O is not separated from CO<sub>2</sub> during the extraction step, the final result includes both N<sub>2</sub>O and CO<sub>2</sub>. For the case of ideal gases,

$$X(ideal)_{CO_2+N_2O} = \frac{n_{CO_2+N_2O}}{n_{total}} = \frac{P_1 V_1 / T_1}{P_2 V_2 / T_2}$$

where  $X_{CO_2}$  is the mole fraction of CO<sub>2</sub> in dry air,  $P_1$ ,  $T_1$ , and  $V_1$  are determined from the small volume, and  $P_2$ ,  $T_2$ , and  $V_2$  are determined from the large volume. In practice, two corrections

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are needed: one for non-ideality using the second Virial coefficients for CO<sub>2</sub> and dry air (Sengers et al., 1971) and a second for nitrous oxide (N<sub>2</sub>O) which is present in the purified CO<sub>2</sub> sample.

Correcting for non-ideality and nitrous oxide:

$$X_{CO_2} = \frac{1}{\phi} \frac{B_2}{B_1} \frac{\left[ 1 - \sqrt{1 + \frac{4P_1 B_1}{RT_1}} \right]}{\left[ 1 - \sqrt{1 + \frac{4P_2 B_2}{RT_2}} \right]} - X_{N_2O}$$

where  $B_1$  is the second Virial coefficient for pure CO<sub>2</sub> at temperature  $T_1$ ,  $B_2$  is the second Virial coefficient for dry, CO<sub>2</sub>-free air at temperature  $T_2$ ,  $\phi$  is the volume ratio, and  $X_{N_2O}$  is the mole fraction of nitrous oxide in the sample.

## 6.2 Manometer Data

Data from a manometer run are stored in a text file. Currently, the data acquisition program stores readings from the pressure sensor and four temperature sensors located inside the oven. The pressure and temperature of the sample ( $P_2$ ,  $T_2$ ) and extracted CO<sub>2</sub> ( $P_1$ ,  $T_1$ ) are determined from an average of 4-10 measurement periods, where each measurement period is ~30 seconds. Data files are stored on the data acquisition computer and also on a system that is regularly backed-up. CO<sub>2</sub> mole fraction is calculated by the data acquisition program, but can also be calculated off-line. Results from each valid manometer run are stored in a database. The operator may abort a run prior to extraction if a stable and consistent CO<sub>2</sub> mole fraction cannot be obtained during the filling steps (see 5.3, step 4d). Results from a run that is aborted or otherwise determined to be invalid should be flagged as such.

## 6.3 Uncertainties

The uncertainty of the WMO mole fraction scale is described in Zhao and Tans (2006). Uncertainties in values assigned to the primary standards are related to imprecision and systematic errors. Sources of uncertainty include: measurements of pressure and temperature, the volume ratio determination, sorption of CO<sub>2</sub> on surfaces, permeability of CO<sub>2</sub> through valve seats, imprecision in the CO<sub>2</sub> extraction step, and uncertainty in the 2<sup>nd</sup> Virial coefficients. Random errors can also be assessed by repeated measurements of the primary standards. The combined uncertainty in the WMO CO<sub>2</sub> scale estimated from repeated measurements of the primaries and an estimate of uncertainties in  $T$ ,  $P$ , and volume ratio is estimated to be 0.069 ppm ( $k=1$ ) (see Zhao and Tans, 2006).

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An update of Zhao and Tans (2006), following methods outlined in JCGM (2008), is currently in progress. Preliminary results indicate that the standard uncertainty of the WMO mole fraction scale is 0.10 ppm ( $k=1$ ), slightly larger than that determined by Zhao and Tans (2006). The main reason for the increase is that the standard uncertainty of the volume ratio is now thought to be larger than first estimated by Zhao and Tans (2006).

### 7.0 CO<sub>2</sub> Calibration Scale

The measurement of CO<sub>2</sub> in primary standards ultimately leads to the establishment of a calibration scale. Here we define the CO<sub>2</sub> calibration scale and how it is updated. The CO<sub>2</sub> mole fraction scale is defined as the manometrically-determined CO<sub>2</sub> mole fractions in a set of 15 primary standards, with CO<sub>2</sub> mole fractions ranging 250 to 520 ppm. The mole fraction of each primary standard is determined based on its entire manometric calibration history, and statistical tests are carried out for potential evidence of drift on every primary standard. The scale is identified as WMO-CO<sub>2</sub>-YYYYY, where YYYY is the year in which the primaries were measured. Scales defined in different years will differ slightly, although differences are typically less than 0.1 ppm (Zhao and Tans, 2006). If a new scale differs by less than 0.02 ppm from its previous named version NOAA/GMD may decide not to change the version number of the new scale. Further, since the scale is propagated to secondary and tertiary standards based on the values assigned to the primaries, any scale can be retroactively propagated. Thus, all measurements of a secondary or tertiary standard performed by a comparative (non-primary) method, regardless of when they were performed, can be expressed on any scale. If a primary standard is retired (e.g. due to drift) a new standard can be added to take its place. New primary standards may also be added to increase the valid range of CO<sub>2</sub> calibration.

### 8.0 Safety

It is GMD policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Pressurized cylinders should be secured (except when they are being weighed). Personal protective equipment (PPE) should be used when working with hazardous chemicals or in a high noise environment.

### 9.0 Documentation

The measured CO<sub>2</sub> mole fraction of each primary standard is recorded in a database along with the date of measurement and other pertinent information. Calibration certificates obtained from accredited testing laboratories (for temperature and pressure sensors, for example) are stored in a 3-ring binder. GMD-issued calibration certificates are not prepared for primary CO<sub>2</sub> standards.

Significant notes relating to the performance and maintenance of the analytical system, including software, should be recorded using ELOG (an electronic record system).

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## 10.0 Appendix

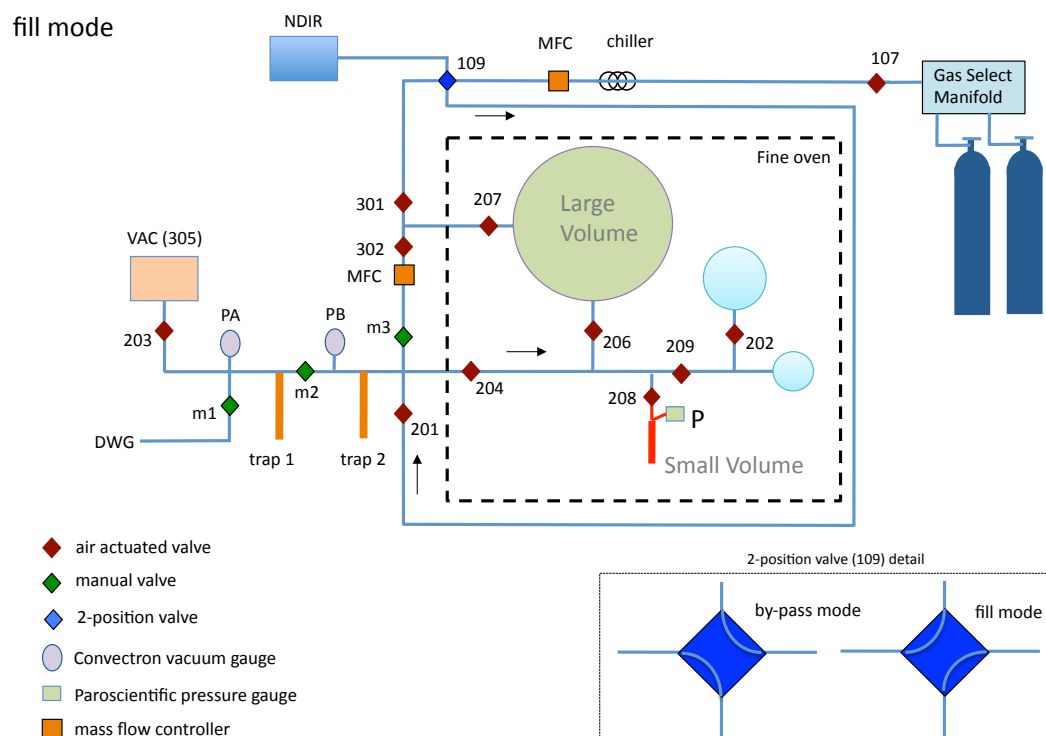
### 10.1 Equipment

The following equipment are critical to the functions described in this TP.

Item	Manufacturer	Model Number
Oven	Yamato	DH62
Valves		
Glass manifold/volumes	custom	
Vacuum gauge (3)	Granville Phillips	Convectron/pirani-type
Vacuum gauge	MKS	120AA-000.1RBJ
Gauge Controller	Granville Phillips	316
Piston Gauge	Ruska	2465A-725
Piston Gauge Autofloat Controller	Ruska	2465A-200
Piston Gauge Mass Set	Ruska	2465A-797
Pressure Gauge	Ruska	7050i
Pressure Gauge	Paroscientific	715
Platinum Resistance Thermometer (2)	Azonix	A12001
Platinum Resistance Thermometer	Hart Scientific	5613
Mass Flow Controller (2)	Edwards	825MF
MFC Controller	Edwards	1605
CO <sub>2</sub> analyzer (NDIR)	Li-Cor	LI-7000
Switch/control unit (2)	HP	3488A
Multimeter	HP	34401A
Multimeter	HP	3478A
Digital Thermometer	Hart Scientific	1529 Chub-E4
Turbo-pump	Varian	Mini-Task
Turbo-pump	Tribodyn	
Alcohol bath	Kinetics	MC480A1
Chart recorder	Linseis	L2005
Computer	HP	300 series
Computer	Dell	

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## 10.2 Drawings



## Technical Procedure: Determination of CO<sub>2</sub> in air using the NOAA manometer

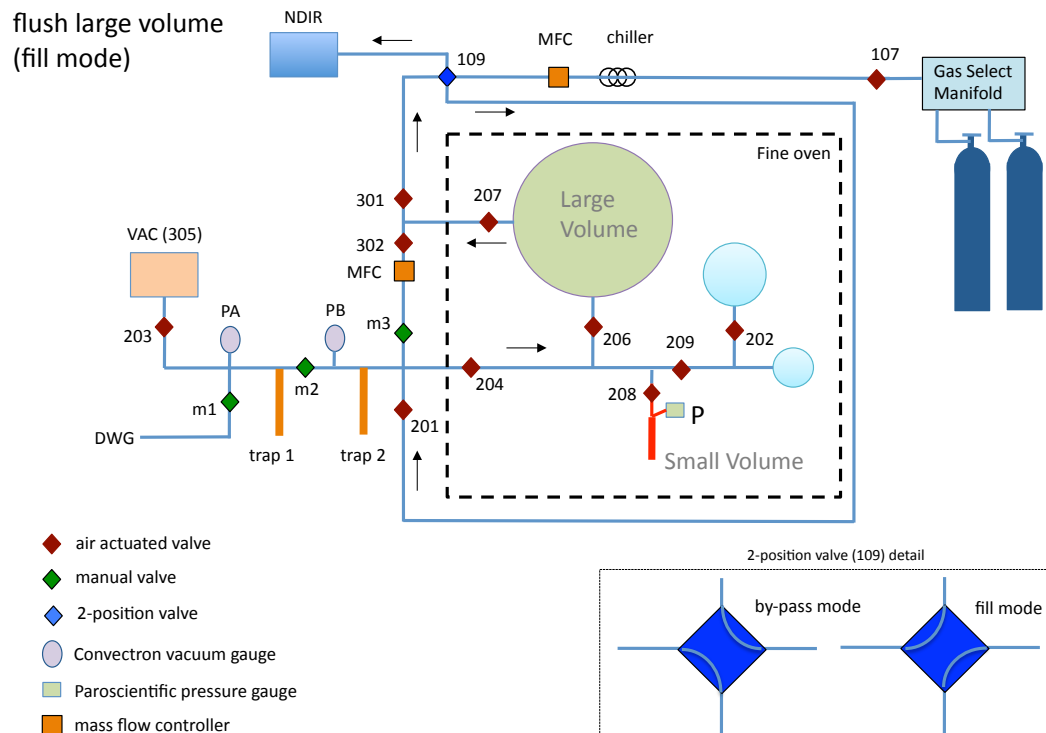


Fig A2. Schematic of NOAA manometer in fill mode, flushing the large volume.

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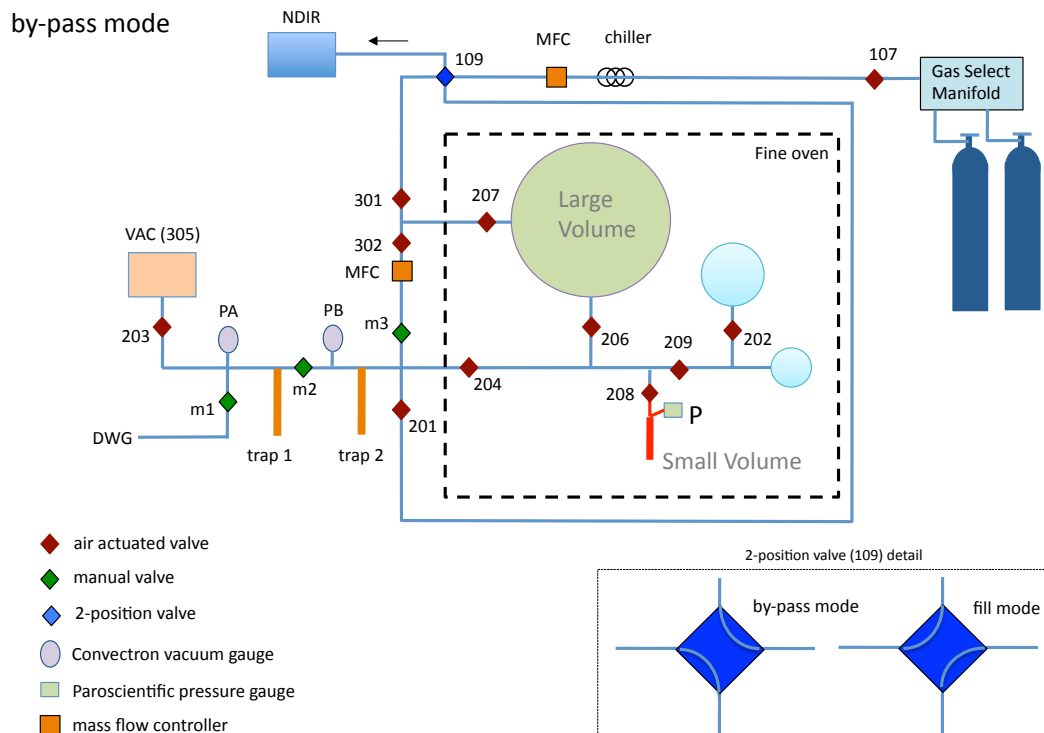


Fig A3. Schematic of NOAA manometer in by-pass mode.

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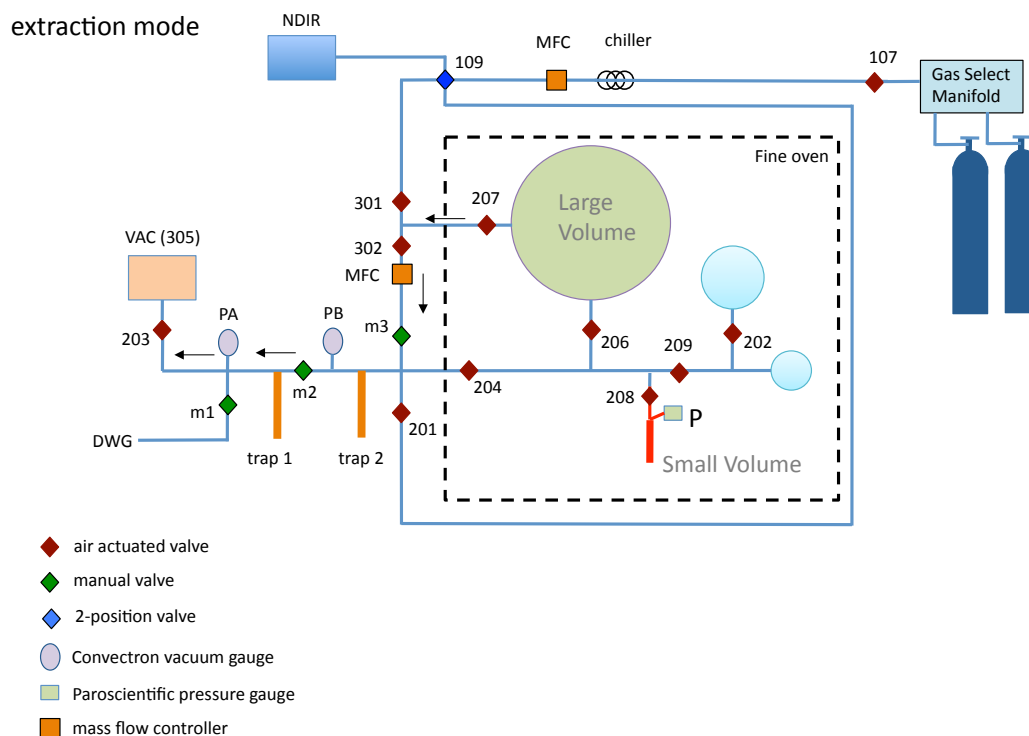


Fig A4. Schematic of NOAA manometer in extraction, or trapping, mode (CO<sub>2</sub>, N<sub>2</sub>O, and water vapor are collected in traps 1 and 2).

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